

PHOTOSYNTHETIC WATER OXIDATION: NEW INSIGHTS FROM X-RAY SPECTROSCOPY

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Nature's process for the conversion of solar to chemical energy begins in Photosystem II (PSII) with the four-electron water oxidation to molecular oxygen, catalyzed by the oxygen evolving complex (OEC). The inorganic core Mn_4CaO_5 goes through four sequential light-driven oxidation reactions, involving states S_0 – S_4 , and molecular oxygen is evolved during the $S_3 \rightarrow [S_4] \rightarrow S_0$ transition. Commonly accepted formal oxidation states of the four Mn ions are $\text{Mn}^{\text{III}}_3\text{Mn}^{\text{IV}}$, $\text{Mn}^{\text{III}}_2\text{Mn}^{\text{IV}}_2$, and $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_3$ for the S_0 , S_1 and S_2 states, respectively, suggesting Mn-based oxidation in each S-state transition. However, the electronic structure of the S_3 state remains contested [1]. Spectroscopic studies suggest Mn-based [2] oxidation during the $S_2 \rightarrow S_3$ transition leading to the formation of an oxo-hydroxo isomer, whereas crystallographic studies suggest ligand-based oxidation resulting in O–O bond formation [3]. Herein, Mn K_α high energy resolution fluorescence detected (HERFD) X-ray absorption spectra (XAS) of S_0 – S_3 states are presented in combination with quantum chemistry simulations. Our results allow for the first time to probe each state in the catalytic sequence based on the pre-edge region and demonstrate Mn-based oxidation in the $S_2 \rightarrow S_3$ transition. These results point to specific O–O bond formation pathways in natural photosynthesis and have implications for the design of synthetic systems.

[1] D. A. Pantazis, *Inorganics* **2019**, 7, 55.

[2] N. Cox, M. Retegan, F. Neese, D. A. Pantazis, A. Boussac, W. Lubitz, *Science* **2014**, 345, 804-808.

[3] M. Suga, et al., *Science* **2019**, 366, 334-338.